

The ambiguous meaning of irreversibility

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Abstract

Irreversibility of spontaneous macroscopic dynamics and its asymmetry with respect to the sign reversal of the variable t is usually interpreted as a genuine property of complex isolated systems. Discussion of the kinetics involved in Joule's experiment concerning spontaneous expansion of a gas shows that the isolation hypothesis results from ambiguous definitions of a number of keywords. Whereas Poincaré's apparent irreversibility result from conservative Hamiltonian dynamics, full relaxation implies interaction with the outside world. Only the latter process leads to entropy change.

1. Introduction

Relating conservative Hamiltonian mechanics valid at the microscopic level to the memory loosing property of relaxations characterizing macroscopic systems remains a challenging exercise. Ambiguous definitions turns this matter into a controversial debate.

Irreversibility is traditionally illustrated by considering a double box, half filled with gas and half evacuated, with a membrane separating the two parts [1]. This is a simplified implementation of Joule's celebrated experiment where he demonstrated that spontaneous expansion of an ideal gas in vacuum from one equilibrium state to a new one occurred without net exchange of heat with the neighbourhood. Comparing the conditions at the start and at the end of the expansion, which are clearly two equilibrium states, but without entering into the detailed mechanism involved, he concluded that there had been no interaction with the environment. Since then

it has been assumed without further discussion that spontaneous relaxation from one equilibrium condition to a new one is a genuine property of isolated systems, the latter term implying strict conservation of energy (elastic collisions with the walls) and matter. In order to evaluate the pertinence of this conclusion, an experiment concerning the dynamics involved is necessary.

2. Joule's experiment

Firing a compressed air pistol in a room is, among others, an adequate experiment to test the dynamics of spontaneous expansion. This may be done either in an acoustic reverberation room or in an anechoic chamber.

In the first case, brutal expansion of the air generates a violent and long lasting acoustic perturbation. In the second case, this is almost absent. The pistol and the air are the same and so are their mechanical properties. The only difference between the two experiments is the nature of the walls. The experiments show therefore unambiguously that the global dynamics leading to final equilibrium implies somewhere interaction with the walls.

In Joule's conclusion, the word "equilibrium" clearly points to conditions reached when the system has been allowed to relax. By this he assumes conditions where all collective motion has died out, including acoustic perturbations.

3. Mechanism

The obvious outcome of the experiment is that the global mechanism of spontaneous expansion of a gas requires at least two steps, one of which implying interaction with the neighbourhood. The kinetics is dominated by the slowest or rate determining step, which is different in the two cases mentioned above.

Depending on the mechanical properties of the walls, the two steps may be almost concomitant or well separated in time. For simplicity, in the discussion to follow it will be assumed that they are separated.

As soon as the constraint defining the initial conditions is removed, a jet is created that turns soon into an acoustic perturbation by reverberation on the walls. The jet is a collective (alias: coherent) motion. Energy borrowed from the thermal supply available at the onset is transferred partially into this motion.

The acoustic perturbation growing by alteration of the jet remains non-thermal, although implying possibly extremely complex molecular trajectories. This modified perturbation may therefore still be given the predicate

collective (or coherent). The transformation is conservative (implies elastic collisions at the walls).

Although the particles of the gas disseminate throughout the volume in a motion that may be chaotic, the memory of the initial conditions is preserved. The amplitude and the phase relation between the components of the acoustic spectrum are its signature.

The final step of the global process concerns destruction of the motion's coherence by collisional exchange of fluctuations with the surrounding thermal bath. Friction and other surface forces causing acoustic absorption by the boundaries belong to the same mechanism. By resolving the correlation present in the collective motion, the energy that had been diverted initially is restored progressively in the system's incoherent thermal bath. At the end of the process, when the new state of equilibrium has been reached, the energy in the thermal bath is as before, giving the illusion that there had been no exchange with the surroundings.

4. Irreversibility

Irreversibility suggests non-recurrence of initial singular events. With macroscopic systems, due to the extremely large Poincaré time, initial dissemination responds perfectly to this definition. In mechanics however, the word bears also a more subtle connotation, indicating that the relevant dynamics is asymmetric with respect to the fictitious sign reversal of the variable t . Let the definitions be labelled respectively “weak” and “strong”. According to them, dissemination governed by Hamiltonian dynamics is weakly irreversible. Being dominated by stochastic interventions of the environment, the second step in the global process is clearly strongly irreversible.

Dissemination of particles under Hamiltonian dynamics has been the object of formal treatment in the recent decennia [2] in the context of ergodic theory and mixing. This has stimulated an abundant literature arguing that chaos generating perturbations justify diffusion-like properties. The logics is however constructed on an alternative criterion for equilibrium where the obvious presence of the collective mode is waved aside. No matter how chaotic the motion may be, Hamiltonian dynamics alone does not remove the strong time correlation inscribed in the motion. An additional mechanism is required. This implies stochastic dissipation to the environment if the system is to reach full thermodynamic equilibrium.

5. Entropy

Boltzmann's entropy is related to the measure of the part of phase space

available to the system. In a microcanonical context, where isolation is assumed, entropy is an explicit function of the collection of extensive properties defining the system's conditions. With a gas at equilibrium, the traditional variables are the energy E , the volume V and the number of particles N . Definition of the entropy may be generalized to non- equilibrium conditions by including the additional constraints as new variables.

In the first step of the relaxation process, work performed by the system on itself by expanding (pdV) converts thermal energy into a collective motion. The intermediate state thereby reached is not at equilibrium. By considering energy contained in the collective mode as the additional variable to be included in the definition of S , it may be shown [4] that the entropy function differentiates as follows:

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \sum_k \frac{\mu_k}{T}dN_k - \frac{1}{T}d(\text{collective energy}).$$

Exact balance of the work performed by the system on itself and the energy increment in the collective mode neutralizes the relevant terms in the latter equation. The initial change is therefore adiabatic ($dS = 0$), in agreement with Liouville's theorem.

At the end of the first period the system is not at equilibrium. Relaxation of the collective mode implies stochastic coherence breaking intervention of the environment. Now the entropy increases while the collective mode progressively vanishes.

5. Conclusion

Relaxation implies two independent steps. The first one is Hamiltonian. No matter how chaotic the motion may be, it is irreversible only in Poincaré's sense. This step is iso- entropic. Joule's experiment shows that the obvious collective transient generated by the initial dissemination requires stochastic intervention of the surroundings for its own relaxation with entropy creation. The source of strong irreversibility is therefore external to relaxing systems.

References

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